

UNCLASSIFIED

Defense Technical Information Center  
Compilation Part Notice

ADP011893

TITLE: Gd[3+]-Yb[3+] Exchange Interactions in LiYb[x]Y[1-x]F<sub>4</sub> Single Crystals

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: International Conference on Solid State Crystals 2000: Growth, Characterization, and Applications of Single Crystals Held in Zakopane, Poland on 9-12 October 2000

To order the complete compilation report, use: ADA399287

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:  
ADP011865 thru ADP011937

UNCLASSIFIED

# Gd<sup>3+</sup>-Yb<sup>3+</sup> exchange interactions in LiYb<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub> single crystals

Lucjan E. Misiak

Department of Experimental Physics, Maria Curie-Skłodowska University, Place Marii Curie-Skłodowskiej 1, 20-031 Lublin, Poland.

## ABSTRACT

The evaluated Gd<sup>3+</sup>-Yb<sup>3+</sup> exchange interactions over the nearest and the next-nearest neighbors in LiYb<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub> are found to increase in parabolic manner with  $x$ , the concentration of Yb<sup>3+</sup> ions. The Gd<sup>3+</sup>-Yb<sup>3+</sup> exchange interactions are sensitive to  $x$  in the range  $x = 0.6 - 1.0$ , while they are almost constant in the range  $x = 0.1 - 0.5$ . The estimated Gd<sup>3+</sup>-Yb<sup>3+</sup> exchange interaction constants ( $J = J_{nn} + J_{nnn}$ ) are in the range 0.5 – 2.8 GHz for  $x$  from 0.1 to 1, respectively. These exchange interaction constants are increased with lowering temperature. The results are comparable to those of estimated using the molecular-field model. The average Gd<sup>3+</sup>-Yb<sup>3+</sup> pair exchange interaction constant is determined to be 0.33 GHz in paramagnetically diluted LiYb<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub> crystals.

**Keywords:** lithium rare-earth fluorides, electron paramagnetic resonance (EPR), exchange interactions, spin-hamiltonian parameters, exchange interaction constant.

## 1. INTRODUCTION

LiYF<sub>4</sub> is the most-used fluoride laser host crystal, generally doped with trivalent rare-earth ions.<sup>1</sup> The LiYF<sub>4</sub> crystals are also used for preparation of infrared and laser windows,<sup>2</sup> to convert infrared excitation to green emission,<sup>3</sup> as well as neutron scintillation detectors.<sup>4</sup> The LiYb<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub> crystals have scheelite (CaWO<sub>4</sub>) structure with the space group  $I4_1/a$  ( $C_{4h}$ ) and the S<sub>4</sub> local symmetry at Y<sup>3+</sup> or Yb<sup>3+</sup> sites, the same as those of LiYF<sub>4</sub> and LiYbF<sub>4</sub>.<sup>5,6</sup> The LiY<sub>1-x</sub>Yb<sub>x</sub>F<sub>4</sub> ( $x = 0 - 1$ ) single crystals doped with Gd<sup>3+</sup> were grown from the melt by a modified Bridgmann-Stockbarger method.<sup>6</sup>

X-band (~9.5 GHz) EPR studies of Gd<sup>3+</sup>-doped LiYF<sub>4</sub> and LiYbF<sub>4</sub> have been reported.<sup>7,8</sup> A detailed X-band EPR study has been performed in Gd<sup>3+</sup>-doped LiYb<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub> crystals, for various values of  $x$  and at variable temperatures, in the range 4.2 - 290 K.<sup>9</sup> Further, the molecular-field model<sup>10</sup> was used to estimate the Gd<sup>3+</sup>-Yb<sup>3+</sup> exchange interactions at 4.2 K. For the host crystals with  $x > 0.1$ , it was not possible to record EPR spectra at temperatures much lower than room temperature, because of increasing line broadening. Detailed Gd<sup>3+</sup> EPR-linewidth studies have also been reported.<sup>11</sup>

The EPR spectrum of Yb<sup>3+</sup> ions was not at all observed, due to the rather short spin-lattice relaxation time of Yb<sup>3+</sup>, which broadens out the Yb<sup>3+</sup> EPR lines substantially at temperatures above 4.2 K; Yb<sup>3+</sup> EPR spectrum was observed only for the host crystals with  $x < 0.2$ . This consisted of a broad line corresponding to the 69% non-magnetic, even-mass isotopes in natural ytterbium with nuclear spin  $I = 0$  (<sup>168</sup>Yb, <sup>170</sup>Yb, <sup>172</sup>Yb, <sup>174</sup>Yb and <sup>176</sup>Yb), at about 4960 G, without any superhyperfine structure. (The Yb<sup>3+</sup> superhyperfine structure was observed<sup>12</sup> in LiYF<sub>4</sub> host crystal, doped by Yb<sup>3+</sup> ions (0.1 at. %) at X-band, for the magnetic field orientation only within 2° from the  $c$  axis.) The spectrum of <sup>171</sup>Yb ( $I = 1/2$ ), with nonzero nuclear magnetic moment in scheelite crystal hosts occurs at X-band in the magnetic field range 8.5 – 10 kG.<sup>13</sup> In LiYb<sub>0.1</sub>Y<sub>0.9</sub>F<sub>4</sub> crystal at 4.2 K only one line was observed at about 9.5 kG.<sup>9</sup>

The nearest-neighbor (nn) Gd<sup>3+</sup> pair spectrum in EuCl<sub>3</sub> have been recorded<sup>14</sup> for the direction of  $\mathbf{H}$  along the  $c$  crystal axis, and the next-nearest neighbor (nnn) Gd<sup>3+</sup> pair spectrum with  $\mathbf{H}$  parallel to the calculated nnn bond direction. In LiYb<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub> crystals, the pair spectrum was not at all observed, neither for  $\mathbf{H}$  parallel to the  $c$  axis, nor for  $\mathbf{H}$  in the XY plane, which contains the bond direction of the nnn Gd<sup>3+</sup> pair. This can be explained to be due to the rather small concentration of the Gd<sup>3+</sup> ions (0.1 - 0.2 mole %) in LiYb<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub>,<sup>9</sup> compared to that in EuCl<sub>3</sub> (0.5 - 1.0 mole % of Gd<sup>3+</sup>).<sup>14</sup> The  $g$  shift of Gd<sup>3+</sup> ion in a paramagnetic LiYb<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub> host, from that in the isostructural diamagnetic LiYF<sub>4</sub> host, is dependent upon the magnetic interactions of the Gd<sup>3+</sup> ion with the Yb<sup>3+</sup> paramagnetic neighbors. These exchange interactions can be estimated from the  $g$  shift values of the Gd<sup>3+</sup> ion in the isostructural paramagnetic and diamagnetic hosts.<sup>8,14</sup>

## 2. ESTIMATION OF $Gd^{3+}$ - $Yb^{3+}$ EXCHANGE INTERACTIONS

The exchange-interaction constant due to the nearest and next-nearest  $Gd^{3+}$  -  $Yb^{3+}$  neighbors in the paramagnetic hosts  $LiYb_xY_{1-x}F_4$  can be evaluated using the shift of the isotropic part of the single-ion g-tensor of a  $Gd^{3+}$  ion, from that in the isostructural diamagnetic host ( $LiYF_4$ ):<sup>8,14</sup>

$$(\delta g_{zz} + \delta g_{xx}) = (g_{zz} + 2g_{xx})_p - (g_{zz} + 2g_{xx})_d = -\frac{96}{\Delta_{av}}(J_{nn} + J_{nnn}). \quad (1)$$

In eq. (1),  $J_{nn}$  and  $J_{nnn}$  are respectively the exchange-interaction constants of  $Gd^{3+}$  with the nearest and next-nearest  $Yb^{3+}$  neighbors, the subscripts p and d refer to the isostructural paramagnetic and diamagnetic hosts  $LiYb_xY_{1-x}F_4$  and  $LiYF_4$ , respectively, and  $\Delta_{av}$  is an average energy difference between the first excited levels and the ground state of  $Yb^{3+}$ . The multilevel spacings,  $\Delta_{av}$ , of these levels from the ground state can be taken into account by averaging.<sup>15</sup>

$$\Delta_{av} = \sum_i \Delta_i \exp(-\Delta_i/k_B T) / \sum_i \exp(-\Delta_i/k_B T). \quad (2)$$

The uncertainty, caused by the averaging, is less than that associated with the experimental measurements.<sup>15</sup> The separations ( $\Delta_i$ ) of the energies between the ground level and the next-three excited states of  $Yb^{3+}$  ion in  $LiYF_4$  crystal<sup>16</sup> are determined to be 212, 364, 455  $cm^{-1}$ , respectively. The average energy separation, to be used in eq. (1) is 294  $cm^{-1}$ . (The other higher-lying levels do not contribute as they are separated from the ground state by large energies,<sup>16</sup> e.g.,  $\sim 10^4 cm^{-1}$ .)

### 2.1. Estimation of $g_{zz}$ and $g_{xx}$

The spin hamiltonian for the  $Gd^{3+}$  ion, occupying a site of local symmetry  $S_4$  in the tetragonal  $LiYb_xY_{1-x}F_4$  host lattice, can be found elsewhere.<sup>9</sup> For the estimation of the  $Gd^{3+}$  -  $Yb^{3+}$  exchange-interaction constant it is necessary to have very accurate values of  $g_{zz}$  and  $g_{xx}$ . These values were usually obtained from least-squares fitting of all the spin Hamiltonian parameters in which a large number of EPR line positions (obtained for several orientations of the external magnetic field) were simultaneously fitted.<sup>9</sup> More precise values of g-factor can be calculated by the use of the experimentally observed line positions for the  $1/2 \leftrightarrow -1/2$  transition (for  $H \parallel Z$  and  $H \parallel X$ ). The calculation to second order using perturbation method, gives<sup>17</sup>

$$g\beta H^{(2)} = h\nu + E \left[ \frac{90}{(1-9y^2)} - \frac{120}{(1-y^2)} \right], \quad (3)$$

where,

$$y = b_2^0 / g\beta H^{(2)}, \quad E = (b_2^0)^2 / 18g\beta H^{(2)}.$$

One can calculate from eq. (3) for  $LiYb_xY_{1-x}F_4$ :

$$g_{zz} = h\nu / \beta H_z^{(2)} \quad \text{and} \quad g_{xx} = h\nu / \beta H^{(2)}(1-A), \quad (4)$$

where,

$$A = \frac{9(b_2^0)^2}{72g_{xx}^2\beta^2(H^{(2)})^2} \left\{ \frac{90}{1 - \left[ \frac{9(b_2^0)^2}{4g_{xx}^2\beta^2(H^{(2)})^2} \right]} - \frac{120}{1 - \left[ \frac{(b_2^0)^2}{4g_{xx}^2\beta^2(H^{(2)})^2} \right]} \right\}. \quad (5)$$

This A value at room temperature can be estimated fairly reasonably by using the  $g_{xx}$  and  $b_2^0$  values, specific to each  $LiYb_xY_{1-x}F_4$  host, determined from least-squares fitting. Thus, when the determined values of A for the various hosts are used in eq. (4) for the evaluation of  $g_{xx}$ , they do not cause significantly large errors. The values of  $g_{zz}$  and  $g_{xx}$ , so computed from eq. (4) for the various hosts, are listed in table 1.

### 2.2. Estimation of the $Gd^{3+}$ - $Yb^{3+}$ exchange interaction constant

The values of the exchange-interaction constant (J), computed using the g shift in eq. (1) are given in table 1. It is seen from Fig. 1 that, as the amount of paramagnetic  $Yb^{3+}$  ions increases for x in the range 0.1 - 1.0, the  $Gd^{3+}$  -  $Yb^{3+}$  exchange-interaction constant J also increases in parabolic manner.

Table 1. The room-temperature values of  $g_{zz}$ ,  $g_{xx}$ ,  $A$ , and  $J$  (the exchange-interaction constant) in  $Gd^{3+}$ -doped  $LiYb_xY_{1-x}F_4$  single crystals. The  $x$  is the mole fraction of  $Yb^{3+}$  ions,  $z$  is the number of nearest and next-nearest neighbors and  $J_p$  ( $= J/z$ ) is the average  $Gd^{3+}$ - $Yb^{3+}$  pair exchange-interaction constant.

$x$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.8	0.9	1.0
$g_{zz}$	1.9956(5)	1.9953(5)	1.9947(5)	1.9947(5)	1.9941(5)	1.9935(11)	1.9920(11)	1.9864(11)	1.9788(11)	1.9738(11)
$g_{xx}$	1.9908(8)	1.9885(8)	1.9866(8)	1.9894(8)	1.9860(8)	1.9855(14)	1.9862(14)	1.9882(14)	1.9863(14)	1.9864(14)
$A$	-0.1165	-0.1173	-0.1188	-0.1171	-0.1188	-0.1186	-0.1185	-0.1161	-0.1165	-0.1169
$J$ (GHz)		0.5(0.30)	0.9(0.30)	0.4(0.3)	1.0(0.3)	1.2(0.6)	1.2(0.6)	1.3(0.6)	2.4(0.6)	2.8(0.6)
$z$	0	1	2	2	3	4	5	6	7	8
$J_p$ (GHz)		0.5	0.45	0.20	0.33	0.30	0.24	0.22	0.34	0.35

In  $LiYbF_4$  the number of each of the nearest-neighbors and the next-nearest neighbors ( $z$ ) is four.<sup>5</sup> As for the  $LiYb_xY_{1-x}F_4$  single crystals, the number of  $z$  can be scaled in proportion to  $x$ , to estimate the average number of  $Yb^{3+}$  neighbors to a  $Gd^{3+}$  ion, and further to calculate the average pair exchange-interaction constant  $J_p$  ( $= J/z$ ). The values of  $J_p$ , so calculated, are included in table 1. It is seen that all the  $J_p$  values are the same (on average 33 GHz), within errors of estimation.

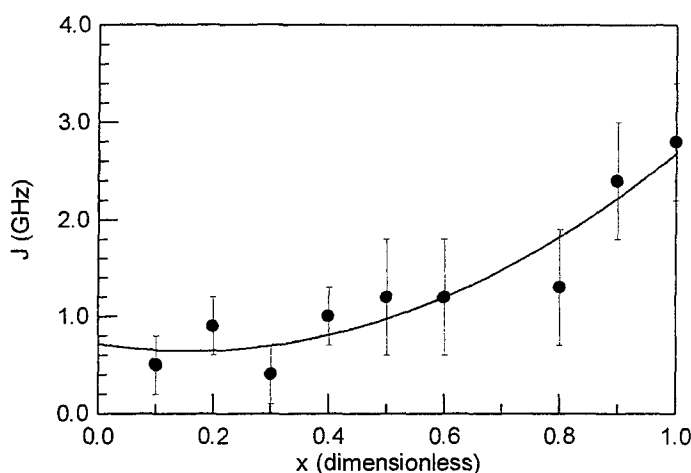


Fig. 1. The exchange-interaction constant ( $J$ ) as a function of the mole fraction of  $Yb^{3+}$  ions ( $x$ ) in  $Gd^{3+}$ -doped  $LiYb_xY_{1-x}F_4$  single crystals.

### 3. DISCUSSION AND COMPARISON OF RESULTS

The calculation of  $Gd^{3+}$ - $Yb^{3+}$  exchange interactions was made previously, using the molecular-field model for  $LiYb_{0.1}Y_{0.9}F_4$  at 4.2 K,<sup>9</sup> because this is the only crystal containing  $Yb^{3+}$  ions, which exhibits well-resolved spectrum at liquid-helium temperature. The values of the  $Gd^{3+}$ - $Yb^{3+}$  exchange-interaction constants  $J$ , at 4.2 K, were calculated to be 3.8 GHz from the molecular-field model<sup>9</sup> and 4.9 GHz in the present calculations. These two values can be considered to be in reasonably good agreement, taking into account the experimental errors and the approximations made in the calculation of  $J$ . The value of  $J$  was estimated to be 6.24 GHz and 2.32 GHz at 77 K and at room temperature, respectively, for  $Gd^{3+}$ - $Eu^{3+}$  exchange interactions in  $Eu(OH)_3$  single crystal.<sup>15</sup> The room-temperature value of  $Gd^{3+}$ - $Eu^{3+}$  exchange interactions (2.32 GHz) is not much different from that of 2.8 GHz, the  $Gd^{3+}$ - $Yb^{3+}$  exchange interactions in  $LiYbF_4$  at room temperature. From the values of  $Gd^{3+}$ - $Yb^{3+}$  exchange interaction constants at room temperature and at 4.2 K in  $LiYb_{0.1}Y_{0.9}F_4$ , and those of estimated for  $Gd^{3+}$ - $Eu^{3+}$  exchange interactions in  $Eu(OH)_3$ ,<sup>15</sup> it is seen that the strength of the exchange interactions increases with decreasing temperature in these hosts. As the temperature decreases, the distances between the ions in the lattice become smaller, thereby enhancing the exchange-interaction constant. This is to be expected, because the exchange interaction constant is determined to be dependent upon an interionic distance  $R$  as  $R^{-12}$ ,<sup>18</sup> or as  $e^{-3.55R}$ ,<sup>19</sup> the latter provides a better agreement to the experimental values of exchange interactions. The exchange interactions between the  $Gd^{3+}$ - $Yb^{3+}$  ions in  $LiYb_xY_{1-x}F_4$  are effected mostly through the ligand  $F^-$  ions.

#### 4. CONCLUSIONS

The  $Gd^{3+}$ - $Yb^{3+}$  exchange-interaction constant  $J$  ( $= J_{nn} + J_{nnn}$ ), as estimated for  $Gd^{3+}$ -doped  $LiYb_xY_{1-x}F_4$  single crystals, are in the range 0.5 - 2.8 GHz at room temperature. On the other hand, at liquid-helium temperature, the calculated value of  $J$  for  $LiYb_{0.1}Y_{0.9}F_4$  is 4.9 GHz. Thus, the exchange-interaction constant is strongly dependent upon temperature, and upon the mole fraction  $x$  (in the range  $x = 0.5 - 1.0$ ). However,  $J$  is almost independent of the mole fraction ( $x$ ) for  $x < 0.5$ . The average  $Gd^{3+}$ - $Yb^{3+}$  pair exchange interaction constant in paramagnetically diluted  $LiYb_xY_{1-x}F_4$  crystals is determined to be 0.33 GHz.

The values of the  $Gd^{3+}$ - $Yb^{3+}$  exchange-interaction constants as estimated in  $LiYb_xY_{1-x}F_4$ , are consistent with those of evaluated using the molecular-field model<sup>9</sup> and are comparable in magnitude to those for  $Gd^{3+}$ - $Eu^{3+}$  exchange constant in  $Eu(OH)_3$  host.<sup>15</sup> Reasonable agreement between the exchange-interaction constants in  $LiYb_xY_{1-x}F_4$  as estimated presently with those of estimated using the molecular-field model, is expected, since the latter is an approximation of the former.

#### REFERENCES

1. E. P. Chicklis, C. S. Naiman, R. C. Folweiler, D. R. Gabbe, H. P. Jensen and A. Linz, "High efficiency room-temperature 2.06  $\mu m$  laser using sensitized  $Ho^{3+}$ : YLF," *Appl. Phys. Lett.* **19**, pp. 119-121, 1971.
2. N. C. Fernelius, G. S. Coble, D. V. Dempsey, J. A. Detrio, J. A. Fox, P. R. Gearson, G. T. Johnston and D. B. O'Quinn, "Multiwavelength laser rate calorimetry on various infrared window materials," in *Emerging Optical Materials, Proc. SPIE Int. Soc. Opt. Eng.* **297**, pp. 137-142, SPIE - The International Society for Optical Engineering, San Diego, 1981.
3. R. K. Watts and W. C. Holton, "Infrared to green conversion in  $LiYF_4$ : Yb, Ho," *Solid State Commun.* **9**, pp. 137-139, 1971.
4. A. R. Spowart, "Evaluation of  $LiYF_4$  as a neutron scintillation detector," *J. Phys. D* **16**, pp. 1819-1822, 1983.
5. R. E. Thoma, G. D. Brunton, R. A. Penneman and T. K. Keenan, "Equilibrium relations and crystal structure of lithium fluorolanthanate phases," *Inorg. Chem.* **9**, pp. 1096-1101, 1970.
6. L. E. Misiak, P. Mikolajczak and M. Subotowicz, "Lithium rare-earth fluoride crystal growth and thermal variation of lattice constants," *Phys. Stat. Sol. A* **97**, pp. 353-359, 1986.
7. Y. Vaills, J. Y. Buzaré and J. Y. Gesland, "Zero-field splittings of  $Gd^{3+}$  in  $LiYF_4$  determined by EPR," *Solid State Commun.* **45**, pp. 1093-1098, 1983.
8. S. K. Misra, M. Kahrizi, P. Mikolajczak and L. E. Misiak, "EPR of  $Gd^{3+}$ -doped single crystals of  $LiYF_4$  and  $LiYbF_4$ :  $Gd^{3+}$ - $Yb^{3+}$  exchange constant," *Phys. Rev. B* **32**, pp. 4738-4741, 1985.
9. L. E. Misiak, S. K. Misra and P. Mikolajczak, "EPR of  $Gd^{3+}$ -doped single crystals of  $LiYb_xY_{1-x}F_4$ ," *Phys. Rev. B* **38**, pp. 8673-8682, 1988.
10. M. R. St. John and R. J. Myers, "Electron-paramagnetic-resonance spectra of ions substituted into transition-metal ion lattices," *Phys. Rev. B* **13**, pp. 1006-1016, 1976.
11. L. E. Misiak, S. K. Misra and U. Orhun, "Study of temperature variation of EPR linewidth of  $Gd^{3+}$ -doped  $LiYb_xY_{1-x}F_4$  single crystals," *Phys. Stat. Sol. B* **154**, pp. 249-258, 1989.
12. J. P. Sattler and J. Namarich, "Electron-paramagnetic-resonance spectra of  $Nd^{3+}$ ,  $Dy^{3+}$ ,  $Er^{3+}$ , and  $Yb^{3+}$  in lithium yttrium fluoride," *Phys. Rev. B* **4**, pp. 1-5, 1971.
13. J. P. Sattler and J. Namarich, "Unusual electron paramagnetic resonance hyperfine spectra of  $Yb^{3+}$  in scheelites," *Phys. Rev. B* **1**, pp. 4256-4261, 1970.
14. R. J. Birgeneau, M. T. Hutchings and W. P. Wolf, "Magnetic interactions between rare-earth ions in insulators. II. Electron-paramagnetic-resonance measurements of  $Gd^{3+}$  pair and  $Gd^{3+}$ - $Eu^{3+}$  interaction constants in  $EuCl_3$ ," *Phys. Rev.* **179**, pp. 275-288, 1969.
15. V. M. Malhotra and H. A. Buckmaster, "A study of the host lattice effect in the lanthanide hydroxides. 34 GHz  $Gd^{3+}$  impurity ion EPR spectra at 77 and 294 K," *Can. J. Phys.* **60**, pp. 1573-1588, 1982.
16. J. E. Miller and E. J. Sharp, "Optical properties and energy transfer in  $LiYF_4$ :  $Nd^{3+}$ ,  $Yb^{3+}$ ," *J. Appl. Phys.* **41**, pp. 4718-4722, 1970.
17. S. K. Misra, "Evaluation of spin hamiltonian parameters from ESR data of single crystals," *Mag. Reson. Rev.* **10**, pp. 285-331, 1986.
18. K. N. Shrivastava and V. Jaccarino, "Variation of superexchange with interatomic distance. I. The  $T_{2g}$  system  $V^{++}-F^- - V^{++}$ ," *Phys. Rev. B* **13**, pp. 299-303, 1976.
19. S. K. Misra and S. Z. Korczak, "EPR of  $Mn^{2+}$  in the Tutton salts  $M(NH_4)_2(SO_4)_2 \cdot 6H_2O$  ( $M = Cd, Co, Ni$ ):  $Mn^{2+}$ - $Ni^{2+}$  exchange interactions," *Phys. Rev. B* **35**, pp. 4625-4632, 1987.